Photoelectron intensity modulation of the Fermi surface on graphite with photon energy

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Abstract

We have measured two-dimensional photoelectron spectroscopy of graphite with various photon energies. We have found that the Fermi surfaces appear at Brillouin zone (BZ) corners independent of photon energy. The photoelectron intensities of the Fermi surfaces were, however, very different even when the photon energies are selected to see the same symmetry planes of BZ. This intensity difference of the Fermi surfaces was well reproduced by considering the "photoemission structure factor" for three-dimensional nature of graphite.

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1. Introduction

As a direct probe for the valence electrons, angle resolved photoelectron spectroscopy (ARPES) has been an indispensable tool for elucidating the electronic structure of various solids. ARPES spectra sometimes showed symmetry-broken patterns due to the matrix element. For example, two-dimensional photoelectron angular distribution (PEAD) from the valence band near the Fermi level of graphite [1-4] showed non six-fold but two-fold symmetry and also non-equivalence among different Brillouin zones (BZ). First, the two-fold symmetry of PEAD in spite of its six-folded crystal structure of graphite was interpreted as the "angular distribution from atomic orbital", indicating that the Fermi surface and the π band of graphite are composed of p_z orbital but not of the p_x or p_y orbital [4]. Next, non-equivalent PEAD among different BZ was understood as the "photoemission structure factor", giving us information about the coefficients for each atomic orbital in the linear combination of atomic orbitals (LCAO) wavefunction [1]. Therefore, ARPES spectra with symmetry-broken PEAD can give us much information not only about the electronic band structure, but also about the orbital character, and even more about the coefficients in the initial state wavefunction.

In order to get more insight, we have performed two-dimensional photoelectron spectroscopy (2D-PES) of single-crystalline graphite taken with various photon energies. Two-dimensional PEAD patterns of the Fermi surface showed significant photon-energy dependence. Considering the three-dimensional nature of graphite, photon-energy dependent PEAD patterns of the Fermi surface were understood.

2. Experiment

2D-PES measurements were performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University [2]. The electric vector of the linearly polarized synchrotron radiation (SR) light was in the horizontal plane. A synthetic graphite single crystal was used for the experiment. The method of sample preparation was described elsewhere [4]. The sample was oriented so that one of the shortest C–C bonds (Γ–M direction) lies horizontally, which is along the electric vector of the normal incident SR. The measurements were performed at room temperature under ultrahigh vacuum of ~1×10^{-8} Pa using a two-dimensional display-type spherical mirror analyzer (DIANA) [5]. Using DIANA, two-dimensional PEAD is efficiently obtained. The PEAD of this experiment was collected by energy window of 300 meV. Typical acquisition time for one PEAD measurement was 30 sec. The total energy resolution was set to 300 - 600 meV depending on the photon energy. The angular resolution was

about 1°. The Fermi level was determined by measuring the photoelectron spectra of gold, which was electrically connected to the sample.

3. Results

Figure 1 shows the series of PEADs of graphite at Fermi level taken with various photon energies. Bright parts correspond to the Fermi surface. The k-traces with various photon energies are shown in Fig. 1(l). Here, free-electron like final states are assumed, where the inner potential V_0 = 14.5 eV [6], the work function ϕ = 4.7 eV [6], and the lattice constant a = 2.46 Å, c = 6.72 Å [7] were used. As reported in Refs. [1, 2], the PEAD of the Fermi surface taken with $h\nu$ = 47.2 eV [Fig. 1(a)] shows two-fold symmetry due to the linear polarization of the incident light and the "angular distribution from atomic orbital". The bright parts appear only at the four left and right corners of the BZ, while the top and bottom corners remain dark. This PEAD is consistent with the fact that the Fermi surface consists of mainly C $2p_z$ atomic orbitals.

With decreasing photon energy from 47.2 eV to 38.2 eV, or changing the k_z from ~$8\pi/c$ to ~$7\pi/c$, the Fermi surface remains at BZ corners (K-H line). The theoretical calculation of graphite showed that the Fermi surface appears only along K-H line. Therefore, this experimental observation is consistent with the theory. However, further decreasing photon energy from 38.2 eV to 29.4 eV, or changing the k_z from ~$7\pi/c$ to ~$6\pi/c$, the Fermi surface almost disappeared around k_z ~ $6\pi/c$. As shown in Fig. 2(a)-(c), the PEAD patterns at the binding energy of 2 eV for k_z ~ 8 π/c, 7 π/c, $6\pi/c$ are clearly seen. Therefore, the only Fermi surface at k_z ~ $6\pi/c$ is hardly seen. This intensity modulation of the Fermi surfaces with photon energy will be discussed below.

The PEAD at the binding energy of 2 eV [Fig. 2(a)-(c)] shows that photoelectrons predominantly appear in the first BZ due to the "photoemission structure factor", as reported in Refs. [1-3]. Note that not only the PEAD pattern in Γ-K-M plane (taken with $h\nu$ ~ 50 eV) [1-3] but also that in A-H-L plane (taken with $h\nu$ ~ 40 eV) shows non-equivalence among different BZ.

As shown in Fig. 2(d)-(f), the energy distribution curve (EDC) near the Fermi level at ~K point was broader than that at ~H point. This is because the π bands are degenerated in A-H-L plane, while they are split-off in Γ-K-M plane.
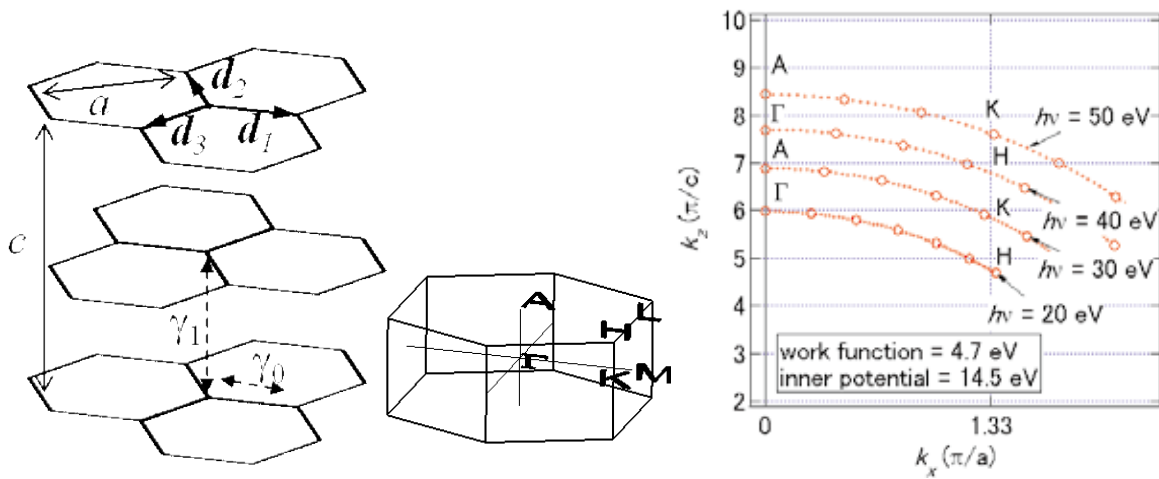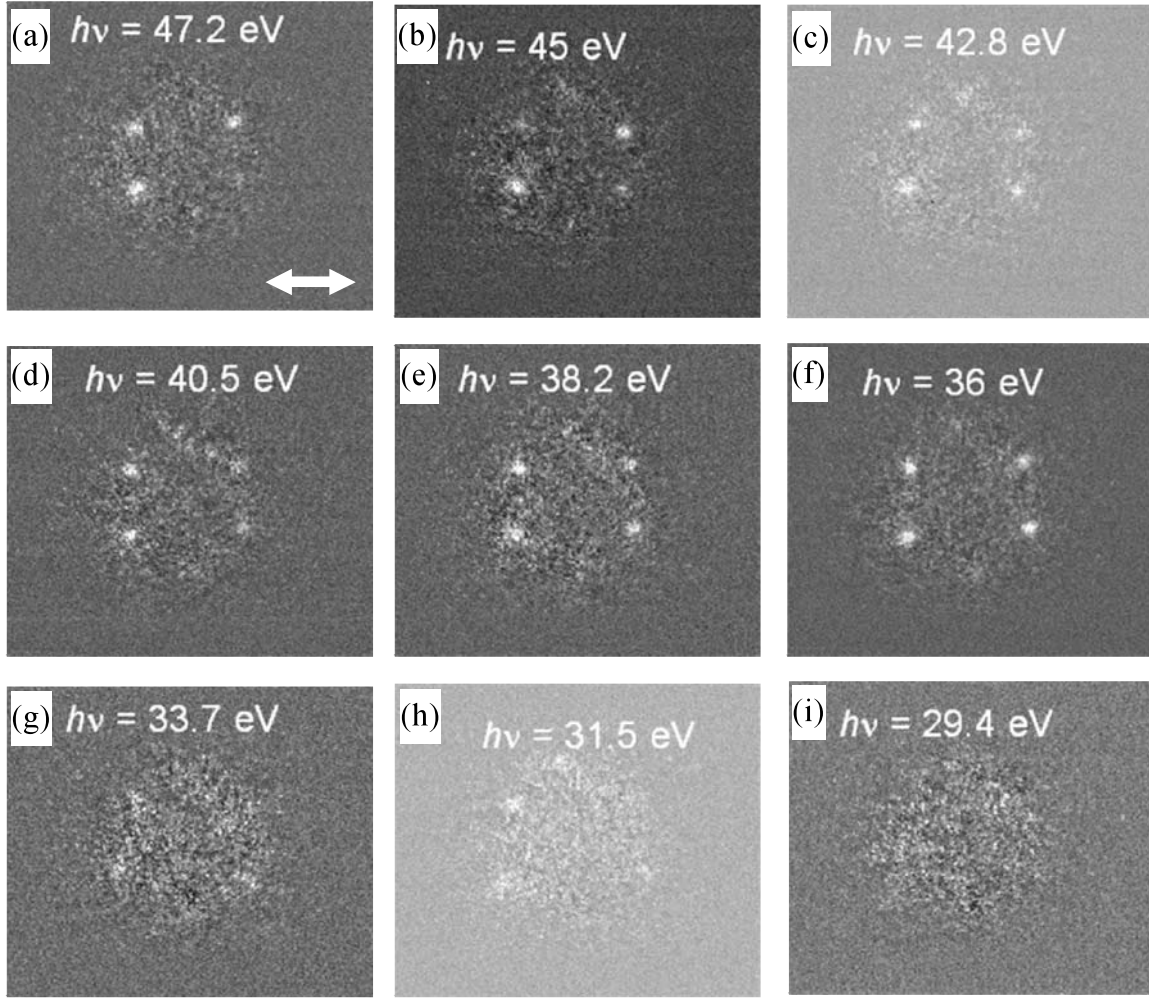
Fig. 1: Fermi surfaces of graphite taken with various photon energies [(a)-(i)]. The electric vector of the linearly polarized SR light is shown in (a). (j) Crystal structure of single-crystalline graphite. (k) First Brillouin zone. (l) Traces in momentum space for various photon energies and emission angles.
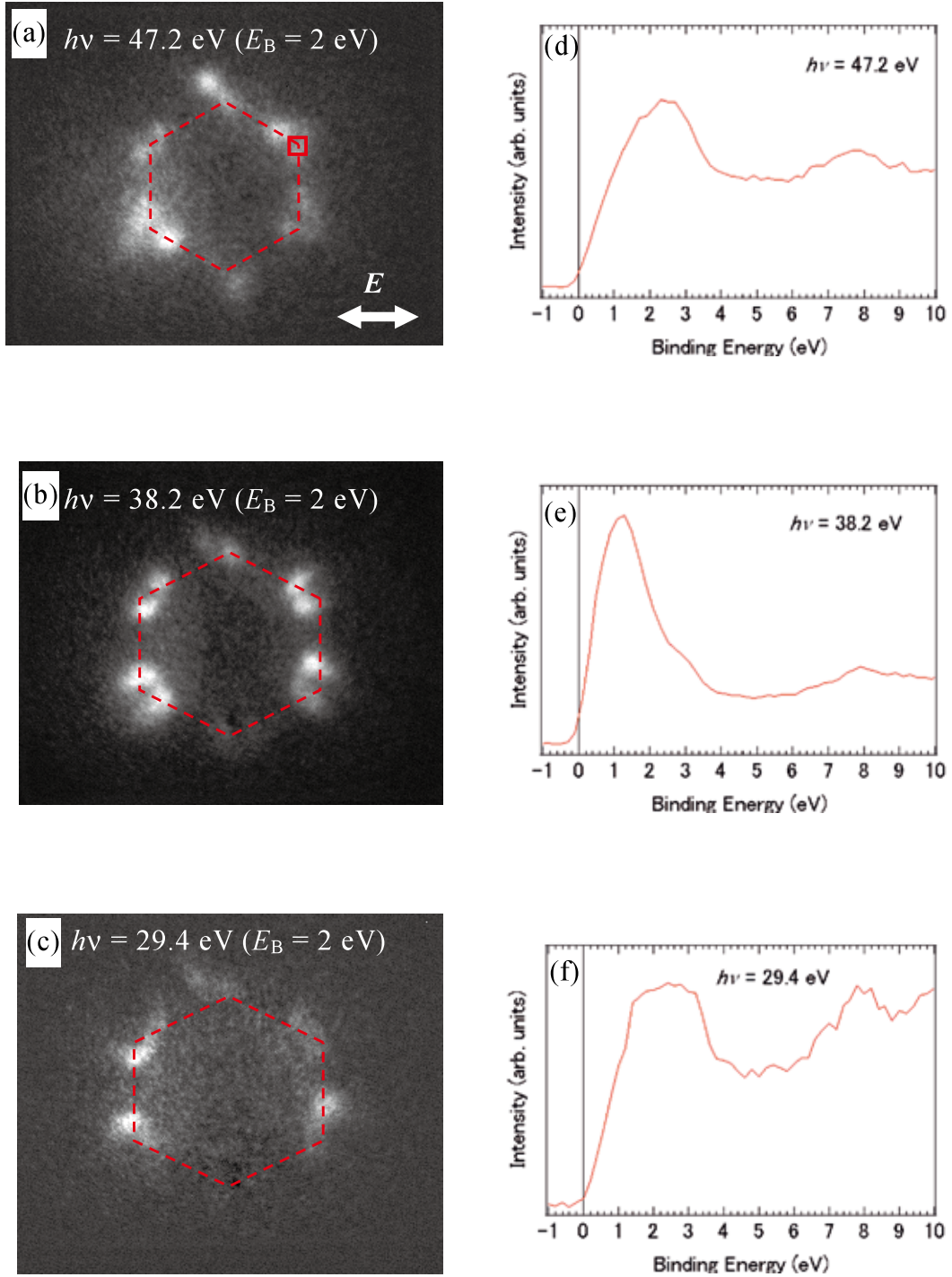
(a) $h\nu = 47.2$ eV ($E_B = 2$ eV)

E

(d) $h\nu = 47.2$ eV

(b) $h\nu = 38.2$ eV ($E_B = 2$ eV)

(e) $h\nu = 38.2$ eV

(c) $h\nu = 29.4$ eV ($E_B = 2$ eV)

(f) $h\nu = 29.4$ eV

Intensity (arb. units)

Binding Energy (eV)

Fig. 2: PEAD patterns at the binding energy of 2 eV with various photon energies [(a)-(c)] and EDCs at the K or H point [(e)-(f)]. The red dashed hexagon indicates the first Brillouin zone. The typical integrated area of EDC at the K or H point is shown as the red square in panel (a).

4. Discussion

The analysis of two-dimensional PEAD from a tight-binding approximated valence band and a Bloch-wave final state showed that the photoelectron intensity $I(\theta, \phi)$ in the direction of polar angle θ and azimuth angle ϕ can be expressed as [8]:

$$I(\theta, \phi) \sim D^1(k_{//})\,|F|^2\,|A_v|^2,$$

where $D^1(k_{//})$ is the one-dimensional density of states, F is the "photoemission structure factor", and A_v is the "angular distribution from the v–th atomic orbital". So far, the analysis was done for the two-dimensional single graphite sheet (graphene) and succeeded to reproduce the experimental PEAD taken with the fixed photon energy of ~50 eV [1, 2]. However, this analysis for the graphene cannot explain the present observation of the intensity modulation of Fermi surface with photon energy, since $D^1(k_{//})$ and F are the same between Fermi surfaces taken with $h\nu \sim 47.2$ eV ($k_z \sim 8\pi/c$) and 29.4 eV ($k_z \sim 6\pi/c$) and A_v does not change so much. Therefore, we have analyzed the PEAD for the graphite including three-dimensional nature.

The tight-binding band-structure calculation for graphite has been done by many groups [7, 9]. There are four non-equivalent carbon atoms in the three-dimensional graphite, as shown in Fig. 1(j). Here, as tight-binding LCAO, four p_z orbitals on non-equivalent atoms were considered. Then, the tight-binding Hamiltonian is expressed as follows:

$$
\begin{pmatrix}
\varepsilon_0 & -\gamma_0\,g^* & 0 & 0 \\
-\gamma_0\,g & \varepsilon_0 & 0 & 2\gamma_1\cos(k_z\,c/2) \\
0 & 0 & \varepsilon_0 & -\gamma_0\,g \\
0 & 2\gamma_1\cos(k_z\,c/2) & -\gamma_0\,g^* & \varepsilon_0
\end{pmatrix}
$$

where ε_0 is energy level of p_z orbital, γ_0 and γ_1 are the transfer-integral for intralayer and interlayer, respectively [see Fig. 1(j)], and $g = \exp(i\mathbf{k}\cdot\mathbf{d}_1) + \exp(i\mathbf{k}\cdot\mathbf{d}_2) + \exp(i\mathbf{k}\cdot\mathbf{d}_3)$. $\mathbf{d}_1$, $\mathbf{d}_2$, and $\mathbf{d}_3$ are position vectors of nearest neighbor carbon atoms shown in Fig. 1(j). For simplicity, only two transfer-integrals (γ_0 and γ_1) were introduced and set as $\gamma_0 = 2.85$ eV, $\gamma_1 = 0.30$ eV, and $\varepsilon_0 = -0.026$ eV [9].

Figure 3 (a)-(c) shows the calculated PEAD patterns of the Fermi surface for three-dimensional graphite (energy window of 300 meV). Note that "angular distribution from the v–th atomic orbital" term, A_v was neglected in order to emphasize the effect of "photoemission structure factor", F for three-dimensional graphite. As in the case of PEAD calculation for two-dimensional graphene [1], the BZ selection

effects are seen even for three-dimensional graphite. That is, photoelectron intensity predominantly appears within the first BZ for any k_z plane. This is also seen in the band structures weighted by the "photoemission structure factor" [Fig. 3(d)-(f)]. The most significant thing is that the calculated PEAD patterns of the Fermi surface for k_z = $8\pi/c$ and $6\pi/c$ are very different even though both are in the same symmetry Γ-K-M plane. In the Γ-K-M plane, the degenerated π bands are split-off. As shown in the electronic bands weighted by the "photoemission structure factor" [Fig. 3(d)-(f)], only one of the π bands can be observed. Moreover, the observable π band is different between k_z = $8\pi/c$ and $6\pi/c$ and the periodicity of the observable π band is $4\pi/c$. This is because the interference effects between the neighboring graphite layers separated by $c/2$ [Fig. 1(j)]. Compared with the experimental observations as shown in Fig. 1, the calculated PEAD patterns well reproduce the intensity modulation of the Fermi surfaces with photon energy, or k_z.

5. Summary

We have performed two-dimensional photoelectron spectroscopy measurements on single-crystalline graphite with various photon energies. The Fermi surfaces were observed at Brillouin zone (BZ) corners independent of photon energy. However, the photoelectron intensities of the Fermi surfaces were very different even when the photon energies were set to the same symmetry planes of BZ. Considering the "photoemission structure factor" for three-dimensional nature of graphite, the intensity modulation of the Fermi surfaces was well reproduced. These results suggest that not only the Brillouin zone symmetry but also the symmetry of the "photoemission structure factor" should be considered appropriately.
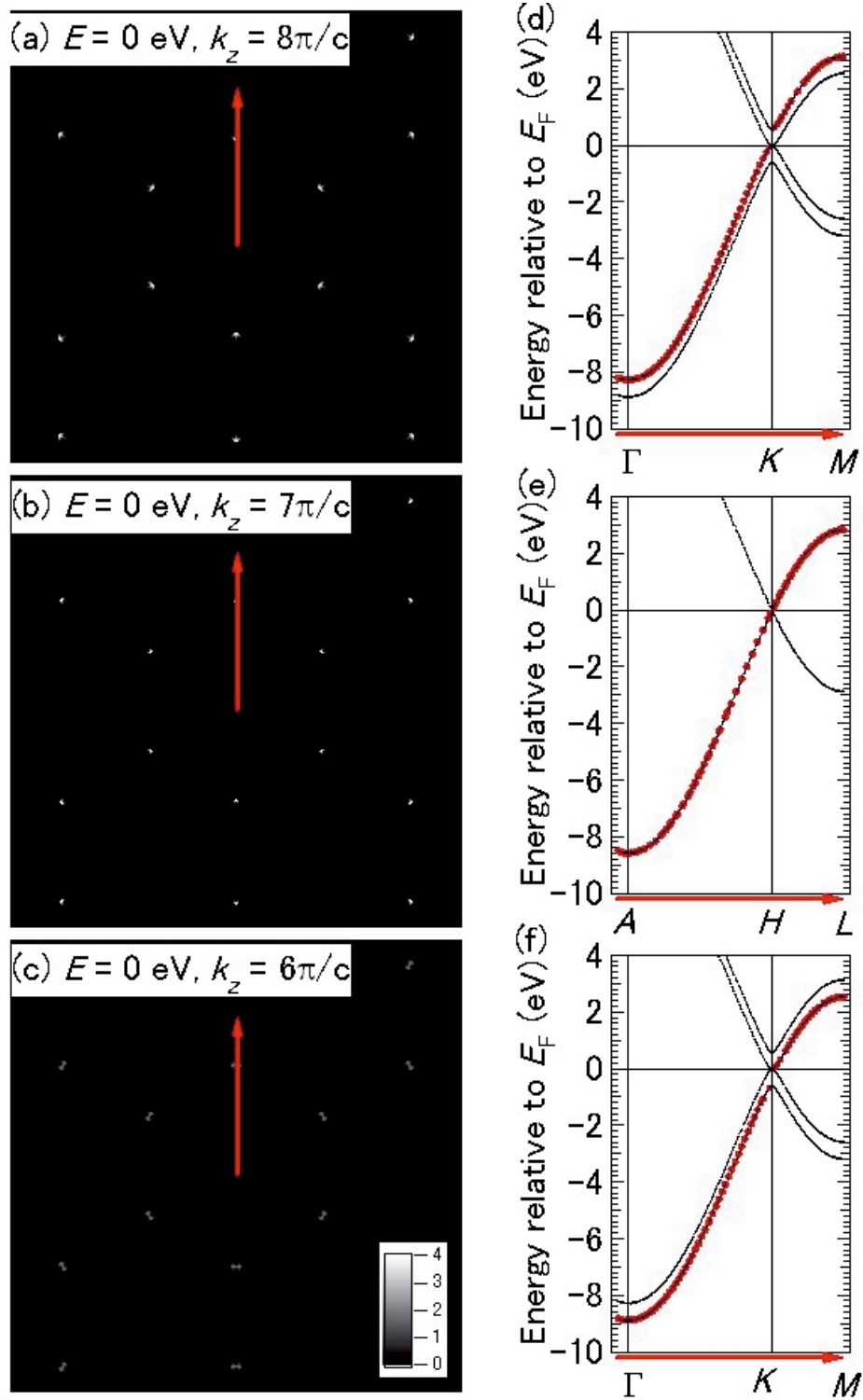
Fig. 3: PEAD patterns of the Fermi surfaces calculated by the tight-binding band-structure calculation [(a)-(c)]. (d)-(f) The band structures along the Γ-K-M or A-H-L line are weighted by the "photoemission structure factor".

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